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**PROCESS FOR SYNTHESIZING BLOCK POLYMERS
BY CONTROLLED RADICAL POLYMERIZATION
FROM DITHIOCARBAMATE COMPOUNDS**

The present invention relates to a novel radical polymerization process for obtaining block copolymers.

Block polymers are usually prepared by ionic
10 polymerization. This type of polymerization has several
drawbacks:

- it only allows the polymerization of certain types of non-polar monomers, especially styrene and butadiene,

15 - it requires a particularly pure reaction mixture and temperatures which are often below room temperature so as to minimize parasitic reactions.

The operational constraints are therefore severe.

Radical polymerization has the advantage of being easily carried out without having to comply with excessive purity conditions, and at temperatures greater than or equal to room temperature. During this polymerization, macroradicals, which have a very short lifetime, recombine irreversibly by coupling or
dismutation. When the polymerization takes place in the presence of several comonomers, the compositional variation of the mixture is infinitely low compared

Consequently, until recently a radical
5 polymerization process allowing block polymers to be
obtained did not exist.

At the present time, several controlled radical polymerization techniques are known, in which the ends of polymer chains may be reactivated in the form of a radical by homolytic bond (for example, C-O or C-halogen) scission.

1. the number of chains is fixed throughout the duration of the reaction,
2. the chains all grow at the same rate, resulting in:

- a linear increase in the molecular masses with conversion,
 - a narrow distribution of masses,
3. the average molecular mass is controlled by the monomer/chain-precursor molar ratio, and

4. the possibility of preparing block copolymers.

The controlled character is even more pronounced when the rate of consumption of the chain precursor is very much greater than the rate of growth of the chains (propagation). There are cases where this is not always true and conditions 1 and 2 are not observed, nevertheless it is always possible to prepare block copolymers.

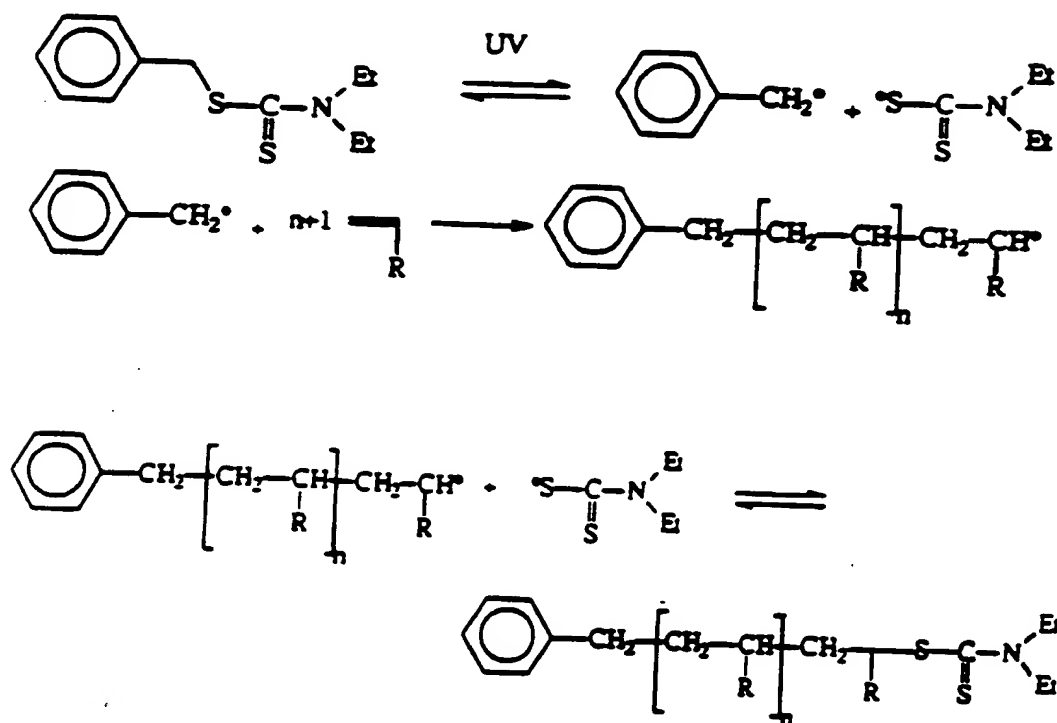
Several approaches have been described for controlling radical polymerization. The most commonly cited consists in introducing, into the mixture, counter radicals which combine reversibly with the growing macroradicals, such as, for example, nitroxyl radicals (Georges et al., *Macromolecules*, **26**, 2987, (1993)). This technique is characterized by high temperatures for labilizing the C-O bond.

Another method, called *Atom Transfer Radical Polymerization*, makes use of transition metal salts combined with organic ligands and an initiator generally consisting of an organic halide; control of the polymerization is made possible by the reversible activation of the C-halogen bond (K. Matyjaszewski, *PCT WO 96/30421*). One drawback with this polymerization is that it requires a stoichiometric quantity of metal per chain precursor.

Otsu (Otsu et al., *Makromol. Chem. Rapid Comm.*, **3**, 127-132, (1982), Otsu et al. *ibid*, **3**, 123-140, (1982), Otsu et al., *Polymer Bull.*, **7**, 45, (1984),

ibid, **11**, 135, (1984), Otsu et al, *J. Macromol. Sci. Chem.*, **A21**, 961, (1984) and Otsu et al., *Macromolecules*, **19**, 2087, (1989)) has shown that certain organic sulphides, particularly

5 dithiocarbamates, allowed chains to be grown in a controlled manner under UV irradiation, according to the principle:



Reaction 1

The principle relies on the photolysis of the C-S bond, which regenerates the carbon macroradical, on the one hand, and the dithiocarbamyl radical, on the other hand. The controlled character of the reaction is due to the reversibility of the C-S bond under UV

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Xanthate disulphides and dithiocarbamate
10 disulphides are themselves well known as transfer
agents in conventional radical polymerization in
thermal mode and in the presence of an initiator, but
no one has hitherto been able to control the
polymerization, or even less to produce block
15 copolymers.

Up till now it was known that disulphides (tetraalkylthiuram disulphide, diisopropylxanthate disulphide and mercaptobenzothiazol disulphide) were activatable thermally or under UV irradiation, whereas monosulphides (substituted xanthates, dithiocarbamates) were activatable only under UV irradiation (Roha et al., *Macromol. Symp.*, **91**, 81-92, (1995), and Okawara et al., *Bull. of the Tokyo Inst. of Techn.*, No. 78, 1966).

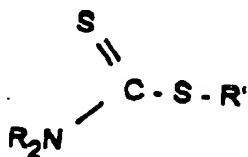
However, controlled radical polymerization making use of a UV irradiation source is very difficult to carry out, especially from an industrial standpoint, since the penetration of the UV photons into the polymerization medium is limited, both by absorption

phenomena (most of the ethylenic monomers absorb in the 210 - 280 nm range) and by diffusion phenomena in disperse media (suspension, emulsion).

Moreover, it has been shown (Turner et al., *Macromolecules*, 23, 1856-1859, (1990)) that photopolymerization in the presence of dithiocarbamate generates carbon disulphide and may be accompanied by a loss of polymerization control.

For these reasons, it has thus been sought to develop a technique which can be used to obtain block copolymers by a process without UV irradiation, preferably by thermal initiation. Until the present time, no controlled radical polymerization system has been able to be demonstrated using dithiocarbamate compounds in the absence of a UV source.

Document WO 98/01478 describes a process for preparing block polymers by controlled radical polymerization. According to that document, such a process cannot be implemented with the aid of compounds, called chain-transfer agents, chosen from dithiocarbamates, of general formula:



Controlled radical polymerization has an advantage over conventional radical polymerization when it is a question of preparing low-molecular-weight

functionalized chains (reactive telomers). Such polymers are desirable for specific applications such as, for example, coatings and adhesives.

Thus, when it is attempted to synthesize chains grafted with, on average, 2 functional comonomers, the fraction of chains with at most one functional site becomes large when the average degree of polymerization is less than a threshold value (e.g. 20 or 30). Controlled radical polymerization makes it possible to reduce, or even to inhibit, the formation of these oligomers having zero or one functional site which degrade the performance in terms of application.

One object of the present invention is to provide a novel controlled radical polymerization process for the synthesis of block polymers from dithiocarbamates.

Another object of the present invention is to provide a novel controlled radical polymerization process for the synthesis of block polymers from dithiocarbamates in the absence of a UV source.

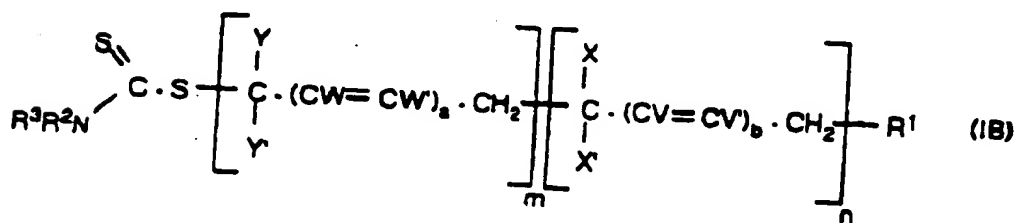
Another object is to provide a controlled radical polymerization process for the synthesis of block polymers from all types of monomers.

Another object is to provide a controlled
25 radical polymerization process for the synthesis of
block polymers containing no metal impurities
deleterious to their use.

Another object is to provide a controlled

Another object is to provide a controlled
5 radical polymerization process for the synthesis of
block polymers and block copolymers having a low
polydispersity index.

To these ends, the invention relates to a process for preparing block polymers of general formula (IA) or (IB):



- R^1 represents:

- 20 • an optionally substituted alkyl, acyl, aryl, alkene or alkyne group (i), or

- an optionally substituted or aromatic, saturated or unsaturated, carbocycle (ii), or
 - an optionally substituted or aromatic, saturated or unsaturated, heterocycle (iii),
- 5 it being possible for these groups and rings (i), (ii) and (iii) to be substituted with substituted phenyl groups, substituted aromatic groups, or groups: alkoxycarbonyl or aryloxycarbonyl (-COOR), carboxyl (-COOH), acyloxy (-O₂CR), carbamoyl (-CONR₂),
- 10 cyano (-CN), alkylcarbonyl, alkylarylcabonyl, arylcarbonyl, arylalkylcarbonyl, phthalimido, maleimido, succinimido, amidino, guanidimo, hydroxyl (-OH), amino (-NR₂), halogen, allyl, epoxy, alkoxy (-OR), S-alkyl, S-aryl, organosilyl, groups having a
- 15 hydrophilic or ionic character, such as the alkali metal salts of carboxylic acids, the alkali metal salts of sulphonic acid, polyalkylene oxide chains (PEO, PPO), cationic substituents (quaternary ammonium salts),
- 20 R representing an alkyl or aryl group,
- Z is an optionally substituted ring comprising a nitrogen atom via which Z is linked to the C(=S)-S-group of formula (IA), the other atoms of the said ring inducing a delocalizing or electron-withdrawing effect
- 25 with respect to the electron density of the nitrogen atom,
- R' and R', which are identical or different, represent:
- an optionally substituted alkyl, acyl, aryl,

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- an optionally substituted or aromatic, saturated or unsaturated, carbocycle (ii), or
- an optionally substituted, saturated or unsaturated, heterocycle (iii),

. substituted phenyl groups or substituted aromatic groups,

arylalkylcarbonyl, phthalimido, maleimido,

groups having a hydrophilic or ionic character, such as the alkali metal salts of carboxylic

R representing an alkyl or aryl group,

25 (ii) and (iii) induce a delocalizing or electron-withdrawing effect with respect to the electron density

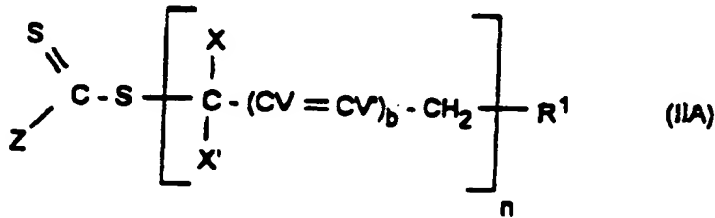
- v, v', w and w' , which are identical or different,

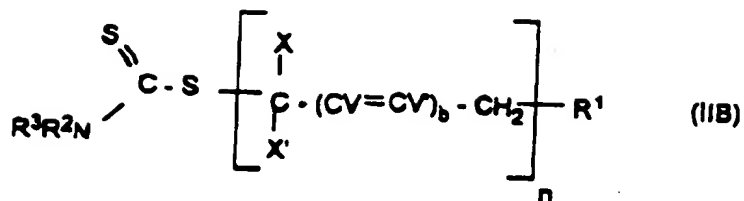
represent: H, an alkyl group or a halogen,

- X , X' , Y and Y' , which are identical or different, represent H, a halogen or a group chosen from R' , OR' , $OCOR'$, $NHCOH$, OH , NH_2 , NHR' , $N(R')_2$, $(R')_2N^+O^-$, $NHCOR'$, CO_2H , CO_2R' , CN , $CONH_2$, $CONHR'$ or $CONR'_2$, in which R' is chosen from alkyl, aryl, aralkyl, alkaryl, alkene or organosilyl groups, optionally perfluorinated and optionally substituted with one or more carboxyl, epoxy, hydroxyl, alkoxy, amino, halogen or sulphonic groups,
- a and b , which are identical or different, are equal to 0 or 1,
- m and n , which are identical or different, are greater than or equal to 1 and, when one or other is greater than 1, the individual repeat units are identical or different,

in which process the following are brought into contact with each other:

- an ethylenically unsaturated monomer of formula:
 $CYY' (=CW-CW')_a = CH_2$,
- a precursor compound of general formula (IIA) or (IIB):





in which Z, X, X', V, V', R¹, R² and R³ have the same meaning, and b and n the same value, as previously, - a radical polymerization initiator.

5 The process therefore consists in bringing into contact with each other a radical polymerization initiator, an ethylenically unsaturated monomer and a precursor of general formula (IIA) or (IIB).

The radical polymerization initiator may be
10 chosen from the initiators conventionally used in radical polymerization. These may, for example, be one of the following initiators:

- hydrogen peroxides such as: *tert*-butyl hydroperoxide, cumene hydroperoxide, *tert*-butyl peroxyacetate, *tert*-butyl peroxybenzoate, *tert*-butyl peroxyoctoate, *tert*-butyl peroxyneodecanoate, *tert*-butyl peroxyisobutyrate, lauroyl peroxide, *tert*-amyl peroxy-pivalate, *tert*-butyl peroxy-pivalate, dicumyl peroxide, benzoyl peroxide, potassium persulphate and
15
20 ammonium persulphate;

- azo compounds such as: 2-2'-azobis(isobutyronitrile), 2,2'-azobis(2-butanenitrile), 4,4'-azobis(4-pentanoic acid), 1,1'-azobis(cyclohexanecarbonitrile), 2-(*tert*-butylazo)-

2-cyanopropane, 2,2'-azobis[2-methyl-N-(1,1)-bis(hydroxymethyl)-2-hydroxyethyl]propionamide, 2,2'-azobis(2-methyl-N-hydroxyethyl]propionamide, 2,2'-azobis(N,N'-dimethyleneisobutyramidine) dichloride,
 5 2,2'-azobis(2-amidinopropane) dichloride, 2,2'-azobis(N,N'-dimethyleneisobutyramide), 2,2'-azobis(2-methyl-N-[1,1-bis(hydroxymethyl)-2-hydroxyethyl]propionamide), 2,2'-azobis(2-methyl-N-[1,1-bis(hydroxymethyl)ethyl]propionamide), 2,2'-
 10 azobis[2-methyl-N-(2-hydroxyethyl)propionamide] and 2,2'-azobis(isobutyramide) dihydrate;

- redox systems including combinations such as:

- . mixtures of hydrogen peroxide or alkyl
 15 peroxide, peresters, percarbonates and the like and of any one of the salts of iron, titanous salts, zinc formaldehyde sulphonylate or sodium formaldehyde sulphonylate, and reducing sugars;
- . alkali-metal or ammonium persulphates,
 20 perborates or perchlorates in combination with an alkali metal bisulphite, such as sodium metabisulphite, and reducing sugars;
- . alkali-metal persulphates in combination with an arylphosphinic acid, such as benzenephosphonic
 25 acid and other similar acids, and reducing sugars.

Preferably, the amount of initiator to be used is determined so that the amount of radicals generated is at most 25 mol% with respect to the amount

As ethylenically unsaturated monomer, the monomers chosen from styrene or its derivatives,

Butadiene and chloroprene correspond to the case in which a and b = 1 in the formulae (IA), (IB), (IIA) or (IIB) and in the formula for the monomer given above.

The vinyl nitriles include more particularly those having from 3 to 12 carbon atoms, such as, in particular, acrylonitrile and methacrylonitrile.

The other ethylenically unsaturated monomers which can be used, alone or as mixtures, or which can

be copolymerized with the above monomers, are, in particular:

- vinyl esters of carboxylic acid, such as vinyl acetate, vinyl Versatate® and vinyl propionate;
- 5 - vinyl halides;
- ethylenically unsaturated monocarboxylic and dicarboxylic acids, such as acrylic acid, methacrylic acid, itaconic acid, maleic acid and fumaric acid, and monoalkyl esters of dicarboxylic
- 10 acids of the type mentioned with alkanols preferably having from 1 to 4 carbon atoms and their N-substituted derivatives;
- amides of unsaturated carboxylic acids, such as acrylamide, methacrylamide,
- 15 N-methylolacrylamide or methacrylamide, and N-alkylacrylamides;
- ethylenic monomers containing a sulphonic acid group and its ammonium or alkali metal salts, for example vinylsulphonic acid, vinylbenzenesulphonic
- 20 acid, α -acrylamidomethylpropanesulphonic acid and 2-sulphoethylene methacrylate;
- amides of vinylamine, especially vinylformamide or vinylacetamide; and
- unsaturated ethylenic monomers containing a
- 25 secondary, tertiary or quaternary amino group, or a heterocyclic group containing nitrogen, such as, for example, vinylpyridines, vinylimidazole, aminoalkyl (meth)acrylates and aminoalkyl (meth)acrylamides such

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as dimethylaminoethyl (meth)acrylate, di-tert-butylaminoethyl (meth)acrylate and dimethylamino(meth)acrylamide. Likewise, it is possible to use zwitterionic monomers such as, for example, 5 sulphopropyl(dimethyl)aminopropyl acrylate.

In order to prepare the copolymers of formula (IA) or (IB) for which $Y = H$ and $Y' = NH_2$, it is preferred to use as ethylenically unsaturated monomers the amides of vinylamine, for example vinylformamide or 10 vinylacetamide. The copolymer obtained is then hydrolysed to acid or basic pH.

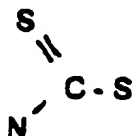
In order to prepare the copolymers of formula (IA) or (IB) for which $Y = H$ and $Y' = OH$, it is preferred to use as ethylenically unsaturated monomers 15 vinyl esters of carboxylic acid such as, for example, vinyl acetate. The copolymer obtained is then hydrolysed to acid or basic pH.

The types and amounts of copolymerizable monomers employed according to the present invention 20 vary depending on the particular final application for which the block polymer is intended. These variations are well known and may be easily determined by those skilled in the art.

In order for the polymer of general formula 25 (IA) or (IB) to be a block polymer, the "precursor" compound of general formula (IIA) or (IIB) must be a polymer. Thus, n is greater than or equal to 1, preferably greater than 5. The monomer units of this

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The essential characteristic of the invention stems from the nature of this precursor of general formula (IIA) or (IIB). This precursor (IIA) or (IIB) forms part of the family of dithiocarbamates, the functional group of which is:



In the case of copolymers of **formula (IA)** or of precursor polymers of **formula (IIA)**, the nitrogen atom of the dithiocarbamate functional group must form part of a ring and the other atoms of the said ring must exhibit an electron-withdrawing effect on the doublet of the nitrogen of the dithiocarbamate functional group.

The nature of this ring Z, comprising the nitrogen of the dithiocarbamate functional group, can vary, given that there is an electron-withdrawing effect on the doublet of the nitrogen.

On account of the process, the multiblock polymers of formula (IA) have the same characteristics with regard to the ring Z.

25 In compounds of formula (IA) and (IIA), the
ring Z is a ring based on carbon atoms.

This carbocycle may include at least one heteroatom other than the nitrogen which links the ring

to $-C(=S)-S-$; this heteroatom may be chosen from O, S, N and/or P. Preferably it is O or N.

The ring Z may be an aromatic or heteroaromatic ring.

5 The ring Z may be functionalized and comprise at least one of the following functional groups: carbonyl (C=O), SO₂, PORⁿ, Rⁿ representing an alkyl, aryl, OR, SR or NR₂ group, where R represents an alkyl or aryl group, these being identical or different.

10 Preferably, the functionalized group is carbonyl.

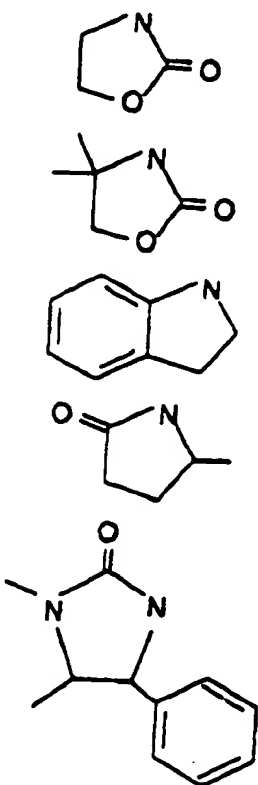
It is also preferable for the functionalized group to be directly linked to the nitrogen of the dithiocarbamate functional group.

The ring Z may be substituted with at least one of the following groups: alkyl, aryl, alkoxy carbonyl or aryloxy carbonyl ($-\text{COOR}$), carboxyl ($-\text{COOH}$), acyloxy ($-\text{O}_2\text{CR}$), carbamoyl ($-\text{CONR}_2$), cyano ($-\text{CN}$), alkyl carbonyl, alkyl aryl carbonyl, aryl carbonyl, aryl alkyl carbonyl, phthalimido, maleimido, succinimido, amidino, guanidino, hydroxyl ($-\text{OH}$), amino ($-\text{NR}_2$), halogen, allyl, epoxy, alkoxy ($-\text{OR}$), S-alkyl, S-aryl, groups having a hydrophilic or ionic character, such as the alkali metal salts of carboxylic acids or the alkali metal salts of sulphonic acid, polyalkylene oxide chains (PEO, PPO), cationic substituents (quaternary ammonium salts), R representing an alkyl or aryl group.

The ring Z may also be substituted with at

least one carbocycle or a heterocycle; this being optionally aromatic and/or substituted with one of the preceding groups. In the latter case, and according to a preferred variant, the ring Z and its cyclic
 5 substituent have two common atoms.

The ring Z is preferably chosen from one of the following rings:



15 Likewise, in the case of copolymers of
 formula (IB) or of precursor polymers of formula (IIB),
 the nitrogen atom of the dithiocarbamate functional
 group must be linked to R^2 and R^1 groups, at least one
 of which induces a delocalizing or electron-withdrawing
 20 effect with respect to the electron density of the

nitrogen atom of the dithiocarbamate functional group.

According to a first variant, R^2 and/or R^3 exert a π withdrawing effect. For this purpose, R^2 and/or R^3 may represent a carbonyl or (hetero)aromatic group.

According to a second variant, R^2 and/or R^3 exert a Σ withdrawing effect. For this purpose, R^2 and/or R^3 may represent an alkyl group substituted with electron-withdrawing groups.

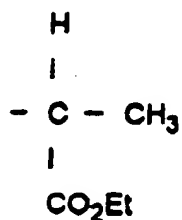
With regard to the substituent R^1 of the compounds of formula (IA), (IB), (IIA) and (IIB), it preferably represents:

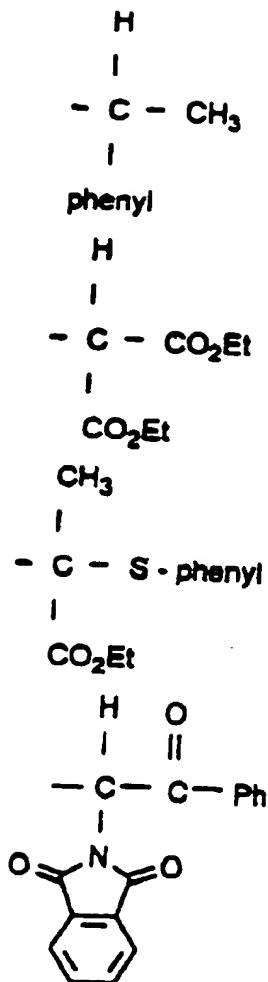
- a group of formula $CR^{11}R^{12}R^{13}$, in which:

- . R^{11} , R^{12} and R^{13} represent groups (i), (ii) or (iii) as defined above, or
- . $R^{11} = R^{12} = H$ and R^{13} is an aryl, alkene or alkyne group,

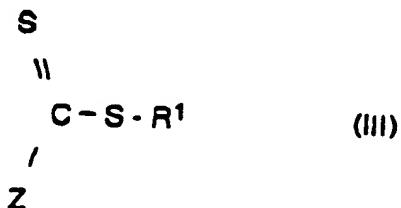
- or a $-COR^{14}$ group in which R^{14} represents a group (i), (ii) or (iii) as defined above.

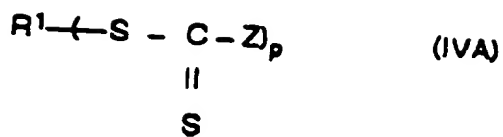
It may especially be chosen from the following groups:





5 The precursor polymer of formula (IIA) may
 come from the radical polymerization of an
 ethylenically unsaturated monomer of formula:
 $\text{CXX}' (= \text{CV} - \text{CV}')_n = \text{CH}_2$, by bringing the said monomer into
 contact with a radical polymerization initiator and a
 10 compound of general formula (IIIA) or (IVA):





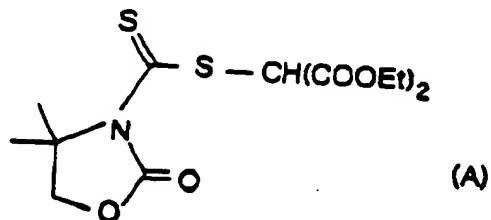
p being between 2 and 10, preferably between 2 and 5.

5 In the general formulae (IIIA) or (IVA), the symbols Z and R¹ have the same meaning as previously. The preferences with regard to its symbols are the same as above.

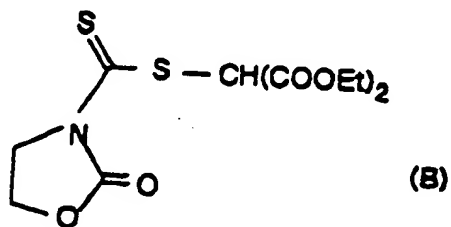
10 Among compounds of formula (IVA), when p = 2, R¹ may be chosen from the groups - CH₂ - phenyl - CH₂ - or - (CH₂)_q -, where q is between 2 and 10.

According to the preferred variants, the compound of formula (IIIA) is chosen from those of the following formulae (A) to (E):

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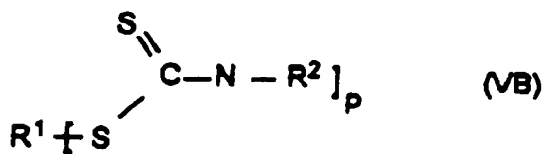
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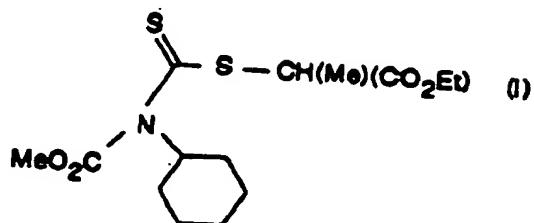


In the general formulae (IIIB), (IVB) or (VB), the symbols R^1 , R^2 and R^3 have the same meaning as previously. The preferences with regard to its symbols

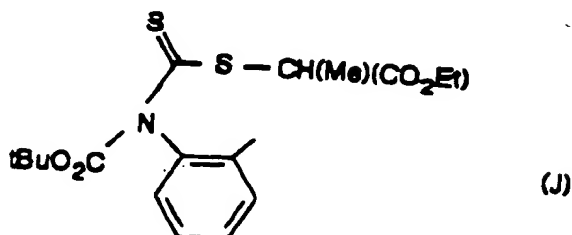
are the same as above.

According to the preferred variants, the compound of formula (IIIB) is chosen from the compounds of the following formulae:

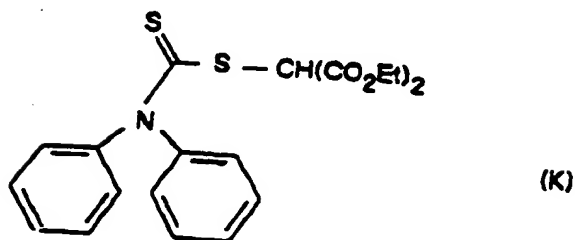
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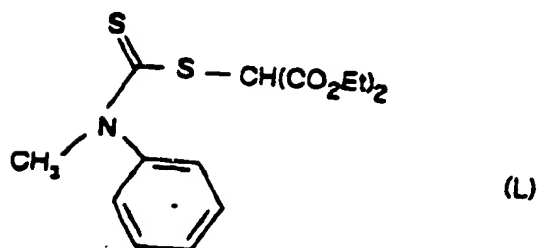
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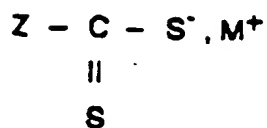


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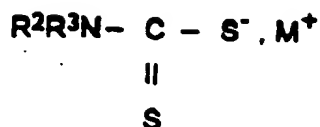
The compounds of formula (IIIA) or (IIIB) are generally obtained by the reaction of the corresponding

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amine with CS₂, so as to obtain the salts of formulae:



5 or



in which M represents sodium, potassium or
10 lithium.

This salt is then brought into contact with a halogen-containing derivative Hal-R¹ (Hal represents Cl, Br or I) in order to give the precursor of formula (IIIA) or (IIIB).

15 During the synthesis of the precursor polymer of formula (IIA) or (IIB), the radical polymerization initiators and the ethylenically unsaturated monomers are of the type of those mentioned previously.

The complete process of synthesizing a block
20 polymer of formula (IA) or (IB) according to the invention may therefore consist in:

(1) synthesizing a polymer by bringing into contact with each other an ethylenically unsaturated monomer of formula: CXX' (=CV-CV')_n=CH₂, a radical
25 polymerization initiator and a compound of formula (IIIA), (IIIB), (IVA), (IVB) or (VB), and

(2) using this polymer obtained at step (1) as precursor of general formula (IIA) or (IIB) in order

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5 This step (2) may be repeated as many times as desired using new monomers to synthesize new blocks and to obtain a multiblock polymer.

Likewise, for the preparation of precursors
15 of formula (IIA) or (IIB) for which $X = H$ and $X' = OH$,
it is preferred to use vinyl esters of carboxylic
acids, such as vinyl acetate for example, as
ethylenically unsaturated monomers. The polymer
obtained is then hydrolysed to acid or basic pH.

25 - different monomers from those of the
previous implementation, and

- instead of the precursor compound of formula (IIA) or (IIB), the block polymer coming from

the previous implementation.

If the implementation is repeated once, a triblock polymer will be obtained, if it is repeated twice, a "quadriblock" polymer will be obtained, and so on. In this way, at each new implementation, the product obtained is a block polymer having an additional polymer block.

Therefore, in order to prepare multiblock polymers, the process consists in repeating, several times, the implementation of the preceding process on the block polymer coming from each previous implementation using different monomers.

According to this method of preparing multiblock polymers, when it is desired to obtain homogeneous block polymers without a composition gradient, and if all the successive polymerizations are carried out in the same reactor, it is essential for all the monomers used in one step to have been consumed before the polymerization of the next step starts, therefore before the new monomers are introduced.

The compounds of formula (IVA) and (IVB) are particularly advantageous as they allow a polymer chain to be grown on at least two active sites. With this type of compound, it is possible to save on polymerization steps in order to obtain an n-block copolymer.

Thus, if $p = 2$, the first block is obtained by the polymerization of a monomer M_1 in the presence

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If p is greater than 2, the process makes it possible to obtain homopolymers or block copolymers whose structure is "multi-branched" or hyperbranched.

The process according to the invention has the advantage of resulting in block polymers having a low polydispersity index.

The invention therefore also relates to the block polymers which can be obtained by the above
25 process.

In general, these polymers have a polydispersity index (PI) of at most 2, preferably of at most 1.5.

5 - polystyrene/polymethyl acrylate,
- polystyrene/polyethyl acrylate,
- polystyrene/poly(*tert*-butyl acrylate),
- polyethyl acrylate/polyvinyl acetate,
- polybutyl acrylate/polyvinyl acetate,
- poly(*tert*-butyl acrylate)/polyvinyl acetate.

Preferably, for these precursor polymers of general formula (IIA) or (IIB), n is greater than or equal to 6.

The following examples illustrate the
20 invention without, however, limiting the scope thereof.

1. SYNTHESIS OF THE PRECURSOR COMPOUNDS OF FORMULA (IIIA) or (IIIB)

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Dissolved in a round-bottomed flask are

10 17.8 g of 2-amino-2-methyl-1-propanol in 100 ml of a
0.1M solution of sodium ethanolate in ethanol. Next,
24 ml of diethyl carbonate are added and the solution
obtained is stirred for 24 hours. The solvent is then
evaporated. After drying, 17.26 g of 5,5-dimethyl-2-
15 oxazolidone are obtained with a yield of 75%.

5.28 g of a 50% dispersion of sodium hydride are washed with pentane and added to this is a THF/DMSO mixture (100 ml THF/100 ml DMSO). This solution is cooled to 0°C and added to it are 11.5 g of 5,5-dimethyl-2-oxazolidone obtained from the first step. The cooling system is interrupted and the reaction mixture is stirred for 1 h 30 minutes and then a white precipitate appears. The temperature is again lowered to 0°C and 1 equivalent of CS₂ (7.6 g) is added. The solution turns a red colour and the stirring is continued until the reaction mixture is perfectly clear (approximately 3 hours). The solution is then taken up in water and extracted with dichloromethane.

The aqueous phase is recovered and added to this are 50 ml of ethanol and 16.2 ml of diethyl chloromalonate. Stirring continues overnight at room temperature and the yellow solution obtained is concentrated in vacuo before being taken up in a saturated aqueous sodium chloride solution. Finally, it is extracted with ether.

7.9 g of dithiocarbamate of formula (A) are isolated by column chromatography. The yield is 23%.

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Example 1.2: Synthesis of dithiocarbamate of formula (B)

2.6 g of a 50% dispersion of sodium hydride are washed with pentane and then introduced into a THF/DMSO mixture (200 ml THF / 200 ml DMSO). Next, 4.35 g of oxazolidone are added and the solution is stirred for an hour at room temperature. A white precipitate appears.

The reaction mixture is then cooled to -20°C and 3.6 ml of CS_2 are added. The solution turns orange and is stirred for 10 minutes at -20°C and then for 2 hours at 0°C . The reaction mixture is again cooled to -20°C and 4 ml of diethyl chloromalonate are added. The solution is stirred for 10 minutes at -20°C , 1 hour at 0°C and 1 hour at room temperature.

The reaction mixture is taken up in ether and

the organic phase is washed with water and then with a saturated sodium chloride solution.

2.6 g of dithiocarbamate of formula (B) are isolated by column chromatography. The yield is 23%.

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Example 1.3: Synthesis of dithiocarbamate of formula (C)

66 g of ephedrine are mixed with 72 g of
10 urea. The mixture is heated at 170°C for 30 minutes and then at 200°C for 2 hours. After cooling to room temperature, 200 ml of water are added. The white precipitate which forms is filtered and washed with a 5% aqueous hydrochloric acid solution and then
15 recrystallized in ethanol. 28 g of 1,5-dimethyl-4-phenyl-2-imidazolidone are obtained with a yield of 37%.

2.6 g of a 50% dispersion of sodium hydride are washed with pentane and a THF/DMSO mixture (200 ml
20 THF / 200 ml DMSO) is added. 9.5 g of 1,5-dimethyl-4-phenyl-2-imidazolidone obtained previously are added and the solution is stirred for 1 hour at room temperature. The reaction mixture is then cooled to 0°C and 3 ml of CS₂ are added. The solution turns orange and
25 is stirred at 0°C for 2 hours. The reaction mixture is taken up in 100 ml of water and extracted with dichloromethane.

The aqueous phase is recovered and 100 ml of ethanol and then 4 ml of diethyl chloromalonate are added. Stirring continues for 2 hours and the reaction mixture is taken up in ethyl acetate. The organic phase
5 thus obtained is washed with water and then with a saturated sodium chloride solution before being concentrated in vacuo.

4.5 g of dithiocarbamate of formula (C) are isolated by column chromatography. The yield is 42%.

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Example 1.4: Synthesis of dithiocarbamate of formula (D)

2.6 g of a 50% dispersion of sodium hydride
15 are washed with pentane and then a THF/DMSO mixture (50 ml THF / 50 ml DMSO) is added. Next, 5.5 ml of indoline are added to the mixture and the solution is stirred for 1 hour at room temperature.

It is then cooled to 0°C and 3.6 ml of CS₂ are
20 added. The solution turns orange and is stirred at 0°C for 2 hours. The reaction mixture is taken up in 100 ml of water and washed with dichloromethane.

The aqueous phase is recovered and 100 ml of ethanol and 6.4 ml of diethyl chloromalonate are added.
25 The solution is stirred for 2 hours and then taken up in ether. The organic phase thus obtained is washed with water and then with a saturated sodium chloride solution before being concentrated.

11 g of dithiocarbamate of formula (D) are isolated by column chromatography in the form of yellow crystals. The yield is 79%.

5 **Example 1.5: Synthesis of dithiocarbamate of formula (E)**

1 g of 5-methyl-2-pyrrolidinone is added to 20 ml of a 1/1 THF/DMSO mixture. 0.56 g of potassium
10 hydroxide and then 1 ml of water and 0.6 ml of CS₂ are added to the solution. The reaction mixture is stirred for 1 hour; the solution turns reddish black.

It is cooled to 0°C and 1 ml of diethyl chloromalonate is added. Stirring is continued for 30
15 minutes at 0°C and then for 2 hours at room temperature. The reaction mixture is taken up in water and extracted with ethyl acetate. The organic phase is recovered and washed with water and then with a concentrated sodium chloride solution before being
20 concentrated in vacuo.

0.86 g of dithiocarbamate of formula (E) is isolated by column chromatography in the form of a yellow oil. The yield is 26%.

25 **Example 1.6: Synthesis of dithiocarbamate of formula (F)**

1.76 g of a 50% dispersion of NaH (30 mmol)

are washed with pentane and then 50 ml of THF and 50 ml of DMSO are added. This solution is cooled to 0°C and then 3.8 g of imidazolidinone (30 mmol) are added. The cold bath is removed.

5 After 1 h 30 min., a white precipitate is formed. The mixture is cooled to 0°C and CS₂ is then added. The solution turns red and stirring continues until the solution is clear (3 hours).

The solution is then hydrolysed using water and extracted with dichloromethane. 200 ml of acetone are added to the aqueous phase followed by 4.2 g of iodine.

After stirring for 2 hours at room temperature, the solution obtained is yellow; it is concentrated in vacuo before being diluted in a saturated NaCl solution and extracted with ether.

Purification of the crude reaction product using column chromatography (heptane/ethyl acetate in a ratio of 9/1) makes it possible to isolate 4.2 g of dimer. The yield is 67%.

2 g of dimer (5.2 mmol) are dissolved in 10 ml of 1,2-dichloroethane. 1.12 g (6.8 mmol) of AIBN are added and the solution is heated at reflux under argon for 6 hours. The solvent is then evaporated and the crude reaction product is purified by column chromatography (dichloromethane/heptane in a ratio of 9/1 and then 7/3). 2.34 g of dithiocarbamate of formula (F) are obtained, i.e. a yield of 33%.

6.8 g of phenylglycinol (50 mmol) are dissolved in a round-bottomed flask containing 50 ml of a 0.2M solution of EtONa in ethanol (prepared by adding 10 mmol of NaH to 50 ml of ethanol). Added to this solution are 6 ml of diethyl carbonate (50 mmol). The solution is stirred for 24 hours and the solvent is then evaporated. The residue is diluted using a saturated aqueous NaCl solution and extracted with ethyl acetate.

0.53 g of a 50% dispersion of NaH (11 mmol) is washed with pentane and then 20 ml of THF and 20 ml of DMSO are added. Next, 1.6 g of oxazolidinone (10 mmol) are added. After 30 minutes of reaction, 200 ml of ether are added, causing two phases to form. The supernatant phase is removed and the residue is taken up in acetone and then precipitated by adding ether. The supernatant phase is again removed.

100 ml of acetone are added to the residue, followed by 1.12 ml (7 mmol) of diethyl chloromalonate. After 3 hours of stirring at room temperature, the

yellow solution obtained is concentrated in vacuo. Next, it is diluted in a saturated NaCl solution and then extracted with ether.

The crude reaction product is purified by column chromatography (heptane/ethyl acetate in a ratio of 7/3); 0.94 g of dithiocarbamate of formula (G) is isolated. The yield is 33%.

Example 1.8: Synthesis of dithiocarbamate of formula (H)

15.5 g of serine methyl ester hydrochloride (100 mmol) are dissolved in a round-bottomed flask containing 140 ml of water. 10.5 g of KHCO_3 (105 mmol) are added and then, after 10 minutes, 14.6 g of K_2CO_3 are added. The solution is cooled to 0°C and then 70 ml of phosgene (133 mmol of a 1.9M solution in toluene) are slowly added over 20 minutes. The solution is stirred overnight at room temperature. Two phases are obtained which are separated; the aqueous phase is evaporated and the residue is taken up in ethyl acetate. The organic phase is concentrated in order to give 14.3 g of intermediate oxazolidinone, i.e. a yield of 99%.

1.45 g of oxazolidinone (10 mmol) are dissolved in 20 ml of DMF and then 1.2 ml (20 mmol) of CS_2 are added. The solution is cooled to 0°C and then 0.48 g (10 mmol) of NaH is added. The solution is

stirred for 30 minutes at 0°C and then for 30 minutes
at room temperature. It is again cooled to 0°C and
0.8 ml (5 mmol) of diethyl chloromalonate is added to
it. After stirring for 30 minutes at 0°C and then for
5 30 minutes at room temperature, the solution is diluted
in ethyl acetate. Next, it is washed with water and
then with brine. The organic phase is concentrated in
vacuo. The crude reaction product is purified by column
chromatography (heptane/ethyl acetate in a ratio of
10 7/3); 1.2 g of dithiocarbamate of formula (H) are
isolated. The yield is 64%.

**Example 1.9: Synthesis of dithiocarbamate of
formula (I)**

15
4.6 ml of cyclohexylamine (40 mmol) dissolved
in 40 ml of ethyl ether are introduced into a round-
bottomed flask and then 5.5 ml of triethylamine
(40 mmol) and 3.5 ml (45 mmol) of methyl chloroformate
20 are added. After three hours of reaction, the solution
is hydrolysed by adding water, the organic phase is
washed with a saturated 1N HCl solution of NaHCO₃ and
then with brine. The organic phase is dried over
magnesium sulphate and concentrated in vacuo in order
25 to give 5.9 g (94%) of intermediate carbamate.

1.57 g (10 mmol) of this intermediate
carbamate are dissolved in 20 ml of DMF and 1.2 ml
(20 mmol) of CS₂ are then added. The solution is cooled

to 0°C and 0.48 g (10 mmol) of a 50% dispersion of NaH is added. After one hour at 0°C, the solution containing the sodium salt is added to a solution of 1.24 ml (9.5 mmol) of ethyl 2-bromopropionate in 20 ml of DMF at 0°C.

After stirring for two hours at room temperature, a yellow solution is obtained which is diluted by adding ethyl ether and hydrolysed by adding water. The organic phase is washed with water and then with brine before being dried and concentrated in vacuo.

The crude reaction product is purified by column chromatography (heptane/ethyl acetate in a ratio of 9/1); 1.6 g of dithiocarbamate of formula (I) are isolated. The yield is 50%.

Example 1.10: Synthesis of dithiocarbamate of formula (J)

0.58 g (3 mmol) of intermediate carbamate (prepared from *o*-toluidine and (Boc)₂O (di-*tert*-butyl dicarbonate)) is dissolved in 10 ml of DMF and then 0.35 ml (6 mmol) of CS₂ is added. The solution is cooled to 0°C and 0.144 g (3 mmol) of a 50% dispersion of NaH is added. After one hour at 0°C, the solution containing the sodium salt is slowly added to a solution of 0.39 ml (3 mmol) of ethyl 2-bromopropionate

in 10 ml of DMF at 0°C.

After stirring for 2 hours at room temperature, the yellow solution obtained is diluted by adding ethyl ether and hydrolysed by adding water. The
5 organic phase is washed with water and then with brine before being dried and concentrated in vacuo.

The crude reaction product is column purified (heptane/ethyl acetate in a ratio of 9/1); 0.68 g of dithiocarbamate of formula (J) is isolated. The yield
10 is 61%.

Example 1.11: Synthesis of dithiocarbamate of formula (K)

15 1.3 equivalents of NaH (1.24 g; 26 mmol) are suspended in 10 ml of THF in a round-bottomed flask placed under argon. 1 equivalent of diphenylamine (3.38 g; 20 mmol) dissolved in a mixture of 18 ml of DMSO and 9 ml of THF is added at 0°C. The colour turns
20 a pale green.

After stirring for one hour, 2.36 equivalents of CS₂ (2.84 ml; 47.2 mmol) are added and the solution becomes orangey yellow. After stirring for 30 minutes, the solution is cooled to -20°C and 1 equivalent of a
25 chlorinated agent (3.20 ml; 20 mmol) is added. The solution is stirred for two hours at room temperature. Next, it is hydrolysed, extracted with ethyl ether and then dried over magnesium sulphate and concentrated in

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Example 1.12: Synthesis of dithiocarbamate of formula (L)

After stirring for one hour, 2.36 equivalents of CS₂ (2.84 ml; 47.2 mmol) are added at 0°C. The solution then becomes brownish red. After stirring for 30 minutes, the solution is cooled to -15°C and 1.20 equivalent of a chlorinated agent (3.20 ml; 20 mmol) is added. The solution becomes brownish yellow; it is stirred for 2 hours at room temperature. Next, it is hydrolysed, extracted with ethyl ether, then dried over magnesium sulphate and concentrated in vacuo.

25 After purification by column chromatography (heptane/ethyl acetate: 9/1), 4.42 g of product are isolated. It is in the form of a yellow oil. The yield is 70%.

2. PREPARATION OF HOMOPOLYMERS of formula (IIA) or (IIB)

These examples demonstrate that the radical
 5 polymerization is controlled by the use of precursors
 of general formula (III). The control character of the
 reaction appears through the values of the
 polydispersity indices $PI = M_w/M_n$, which are less than
 1.5, and the values of the number-average molecular
 10 mass M_n , which are close to the theoretical values and
 expressed by the following formula:

$$M_n = \frac{M_m \cdot x}{M_p \cdot 100} M_{mol}$$

where: M_n : moles of monomer

M_p : moles of precursor of formula (III)

x: conversion of the monomer (%)

15 M_{mol} : molecular mass of the monomer (g/mol).

Example 2.1: Styrene homopolymer

Introduced into a 10 ml round-bottomed flask
 are:

20 - 1 mmol of dithiocarbamate of formula (A)
 (0.35 g) and

- 40 mmol of styrene (4.16 g).

The temperature is raised to 95°C and
 0.03 mmol of lauroyl peroxide (12.8 mg) is added. The
 25 polymerization lasts 12 hours, during which 0.02 mmol

of lauroyl peroxide is added every two hours.

The polymer is recovered by evaporating the traces of residual monomer and analysed by GPC in a THF medium and in polystyrene equivalents.

5 GPC analysis of the homopolymer obtained above allows its number-average mass M_n to be measured. It also allows its weight-average mass (M_w) to be measured and hence the polydispersity index (PI), corresponding to the ratio of M_w to M_n .

10 The results are as follows:

- degree of conversion: 43%,
- average molecular mass $M_n = 3500$,
- polydispersity index $PI = 1.1$.

15 **Example 2.2: methyl acrylate homopolymer**

Introduced into a round-bottomed flask are:

- 1 mmol of dithiocarbamate of formula (A) (0.35 g) and

- 20 - 40 mmol of methyl acrylate (3.44 g).

The temperature is raised to 80°C and 0.03 mmol of lauroyl peroxide (12.8 mg) is added. The polymerization lasts 6 hours during which 0.02 mmol of lauroyl peroxide is added every two hours.

25 The polymer is recovered by evaporating, under vacuum, the traces of residual monomer and analysed by GPC in THF medium and in polystyrene equivalents:

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- For each tube, the polymer is recovered by evaporating the toluene and the residual monomer; it is analysed by GPC in THF medium. The masses are given in polystyrene equivalents. The results obtained are given in Table 1.

Table 1

Time (min.)	Conversion (%)	M_n	PI
63	6.6	770	(*)
126	14.4	1260	(*)
240	27.4	1700	1.2
359	37.2	2200	1.2
1443	80.0	4400	1.2

(*): part of the mass distribution is outside the calibration; the polydispersity index for these 5 specimens cannot therefore be calculated.

Example 2.4: ethyl acrylate homopolymer / polymerization kinetics

10 A stock solution is prepared by mixing:

- 5.533 g of ethyl acrylate,
- 0.241 g of dithiocarbamate of formula (A)

and

- 11.3 mg of azobis(isobutyronitrile) (AIBN).

15 Aliquots of about 10 g of this solution are dispensed in tubes and heated to 70°C. The polymerizations in tubes are stopped at different times by cooling and introducing 4 ml of toluene containing 25 mg of hydroquinone.

For each tube, the polymer is recovered by evaporating the toluene and the residual monomer; it is analysed by GPC in THF medium. The masses are given in polystyrene equivalents. The results obtained are given in Table 2.

Table 2

Time (min.)	Conversion (%)	M_n	PI
31	1.9	323	(*)
49	15.6	2100	1.7
101	50.6	4300	1.6
150	63.5	5300	1.5
211	77.2	5900	1.6

(*): part of the mass distribution is outside the calibration; the polydispersity index for this specimen cannot therefore be calculated.

Example 2.5: styrene homopolymer

Introduced into a round-bottomed flask are:

- 2.23 g of styrene,
- 84.5 mg of dithiocarbamate of formula (B)

and

- 4.2 mg of lauroyl peroxide.

The temperature is raised to 110°C. The reaction lasts 24 hours during which several additions

of lauroyl peroxide are made:

- 4.7 mg after 2 hours,
- 4.1 mg after 4 hours.

The polymer is recovered by evaporating,
5 under vacuum, the traces of residual monomer and
analysed by GPC in THF medium and in polystyrene
equivalents:

- degree of conversion: 98.1%,
- average molecular mass $M_n = 8500$,
- 10 - polydispersity index $PI = 1.3$.

Example 2.6: ethyl acrylate homopolymer

Introduced into a round-bottomed flask are:

- 15 - 2.13 g of ethyl acrylate,
- 84.5 mg of dithiocarbamate of formula (B)

and

- 4.5 mg of lauroyl peroxide.

The temperature is raised to 80°C. The
20 reaction lasts 24 hours during which several additions
of lauroyl peroxide are made:

- 5.0 mg after 2 hours,
- 3.8 mg after 4 hours.

The polymer is recovered by evaporating,
25 under vacuum, the traces of residual monomer and
analysed by GPC in THF medium and in polystyrene
equivalents:

- degree of conversion: 97.5%,
- average molecular mass $M_n = 10,700$,
- polydispersity index $PI = 1.2$.

5 **Example 2.7: vinyl acetate homopolymer**

Introduced into a round-bottomed flask are:

- 1.82 g of vinyl acetate,
- 85.1 mg of dithiocarbamate of formula (B)

10 and

- 8.8 mg of lauroyl peroxide.

The temperature is raised to 80°C. The reaction lasts 24 hours during which several additions of lauroyl peroxide are made:

- 15
 - 8.1 mg after 2 hours,
 - 8.0 mg after 4 hours.

The polymer is recovered by evaporating, under vacuum, the traces of residual monomer and analysed by GPC in THF medium and in polystyrene

20 equivalents:

- degree of conversion: 59.2%,
- average molecular mass $M_n = 4600$,
- polydispersity index $PI = 2.0$.

25 **Example 2.8: styrene homopolymer**

Introduced into a round-bottomed flask are:

- 2.24 g of styrene,
- 0.113 g of dithiocarbamate of formula (C)

and

- 4.5 mg of lauroyl peroxide.

5 The temperature is raised to 110°C. The reaction lasts 24 hours during which several additions of lauroyl peroxide are made:

- 4.7 mg after 2 hours,
- 3.6 mg after 4 hours.

10 The polymer is recovered by evaporating, under vacuum, the traces of residual monomer and analysed by GPC in THF medium and in polystyrene equivalents:

- degree of conversion: 98.0%,
- 15 - average molecular mass $M_n = 7600$,
- polydispersity index $PI = 1.6$.

Example 2.9: ethyl acrylate homopolymer

20 Introduced into a round-bottomed flask are:

- 2.13 g of ethyl acrylate,
- 0.115 g of dithiocarbamate of formula (C)

and

- 4.3 mg of lauroyl peroxide.

25 The temperature is raised to 80°C. The reaction lasts 24 hours during which several additions of lauroyl peroxide are made:

- 4.6 mg after 2 hours,
- 4.9 mg after 4 hours.

The polymer is recovered by evaporating, under vacuum, the traces of residual monomer and analysed by GPC in THF medium and in polystyrene equivalents:

- degree of conversion: 95.2%,
- average molecular mass $M_n = 8600$,
- polydispersity index $PI = 1.4$.

Example 2.10: vinyl acetate homopolymer

Introduced into a round-bottomed flask are:

- 1.84 g of vinyl acetate,
 - 0.112 g of dithiocarbamate of formula (C)
- and
- 8.3 mg of lauroyl peroxide.

The temperature is raised to 80°C. The reaction lasts 24 hours during which several additions of lauroyl peroxide are made:

- 8.8 mg after 2 hours,
- 8.0 mg after 4 hours.

The polymer is recovered by evaporating, under vacuum, the traces of residual monomer and analysed by GPC in THF medium and in polystyrene equivalents:

- degree of conversion: 33%,

- average molecular mass $M_n = 2500$,
- polydispersity index $PI = 1.4$.

Example 2.11: styrene homopolymer

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Introduced into a round-bottomed flask are:

- 2.23 g of styrene,
- 95.1 mg of dithiocarbamate of formula (D)

and

10

- 4.1 mg of lauroyl peroxide.

The temperature is raised to 110°C. The reaction lasts 24 hours during which several additions of lauroyl peroxide are made:

15

- 4.2 mg after 2 hours,
- 3.9 mg after 4 hours.

The polymer is recovered by evaporating, under vacuum, the traces of residual monomer and analysed by GPC in THF medium and in polystyrene equivalents:

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- degree of conversion: 97.6%,
- average molecular mass $M_n = 6800$,
- polydispersity index $PI = 2.0$.

Example 2.12: ethyl acrylate homopolymer

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Introduced into a round-bottomed flask are:

- 2.15 g of ethyl acrylate,

and

The temperature is raised to 80°C. The

- 4.5 mg after 2 hours,

The polymer is recovered by evaporating,

- degree of conversion: 91.8%,

- average molecular mass $M_n = 7900$,

- polydispersity index $PI = 1.6$.

Introduced into a round-bottomed flask are:

- 2.23 g of styrene,

- 87 mg of dithiocarbamate of formula (E) and

- 4.0 mg of lauroyl peroxide.

The temperature is raised to 110°C. The

- 4.6 mg after 2 hours,

- 4.6 mg after 4 hours.

- degree of conversion: 97.1%,
- average molecular mass $M_n = 8300$,
- polydispersity index $PI = 1.4$.

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- 2.13 g of ethyl acrylate,
- 88.5 mg of dithiocarbamate of formula (E)

15

The temperature is raised to 80°C. The

- 4.5 mg after 2 hours,

- 4.5 mg after 4 hours.

25

- degree of conversion: 94.4%,
- average molecular mass $M_n = 9700$,
- polydispersity index $PI = 1.2$.

5

and

- 10 of lauroyl peroxide are made:

- The polymer is recovered by evaporating, under vacuum, the traces of residual monomer and analysed by GPC in THF medium and in polystyrene equivalents:

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(33.8 mg) .

The tube is closed by a screw stopper and

then immersed in an oil bath preheated to 80°C. The polymerization lasts 24 hours.

The polymer is recovered by evaporating the traces of residual monomer and analysed by GPC in THF medium and in polystyrene equivalents. The results obtained are as follows:

- degree of conversion: 61%,
- number-average molar mass $M_n = 5600$,
- polydispersity index $PI = 1.4$.

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Example 2.17: styrene homopolymer

Introduced into a glass tube are:

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- 0.014 mmol of AIBN (2.3 mg),
- 10 mmol of styrene (1.03 g) and
- 0.12 mmol of dithiocarbamate of formula (F) (32 mg).

The tube is closed by a screw stopper and then immersed in an oil bath preheated to 115°C. The polymerization lasts 24 hours.

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The polymer is recovered by evaporating the traces of residual monomer and analysed by GPC in THF medium and in polystyrene equivalents. The results obtained are as follows:

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- degree of conversion: 95%,
- number-average molar mass $M_n = 7200$,
- polydispersity index $PI = 1.19$.

Example 2.18: methyl methacrylate homopolymer

Introduced into a glass tube are:

- 0.012 mmol of AIBN (2 mg),
- 5 - 10 mmol of ethyl acrylate (1 g),
- 0.12 mmol of dithiocarbamate of formula (F)
(31.7 mg) and
- 1 g of methyl ethyl ketone.

The tube is closed by a screw stopper and
10 then immersed in an oil bath preheated to 80°C. The
polymerization lasts 24 hours.

The polymer is recovered by evaporating the
traces of residual monomer and analysed by GPC in THF
medium and in polystyrene equivalents. The results
15 obtained are as follows:

- degree of conversion: 96%,
- number-average molar mass $M_n = 13,900$,
- polydispersity index $PI = 1.64$.

20 Example 2.19: vinyl acetate homopolymer

Introduced into a glass tube are:

- 0.026 mmol of AIBN (2 mg),
- 10 mmol of vinyl acetate (0.86 g) and
- 25 - 0.12 mmol of dithiocarbamate of formula (G)
(48 mg).

The tube is closed by a screw cock and then
immersed in an oil bath preheated to 80°C. The

5 as follows:

5 as follows:

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Introduced into a glass tube are:

- 15

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- degree of conversion: 62%,
- number-average molar mass $M_n = 7500$,
- polydispersity index $PI = 1.39$.

Example 2.21: styrene homopolymer

Introduced into a glass tube are:

- 0.013 mmol of AIBN (2.1 mg),
- 10 mmol of styrene (1.04 g) and
- 0.12 mmol of dithiocarbamate of formula (G) (48 mg).

The tube is closed by a screw stopper and then immersed in an oil bath preheated to 115°C. The polymerization lasts 24 hours.

The polymer is recovered by evaporating the traces of residual monomer and analysed by GPC in THF medium and in polystyrene equivalents.

- degree of conversion: 95%,
- number-average molar mass $M_n = 5300$,
- polydispersity index $PI = 1.28$.

Example 2.22: vinyl acetate homopolymer

Introduced into a glass tube are:

- 0.026 mmol of AIBN (4.2 mg),
- 10 mmol of vinyl acetate (0.86 g) and
- 0.13 mmol of dithiocarbamate of formula (H) (48 mg).

The tube is closed by a screw stopper and then immersed in an oil bath preheated to 80°C. The polymerization lasts 24 hours.

The polymer is recovered by evaporating the traces of residual monomer and analysed by GPC in THF medium and in polystyrene equivalents. The results are as follows:

- 5
- degree of conversion: 60%,
 - number-average molar mass $M_n = 4700$,
 - polydispersity index $PI = 1.91$.

Example 2.23: ethyl acrylate homopolymer

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Introduced into a glass tube are:

- 0.013 mmol of AIBN (2.1 mg),
 - 10 mmol of ethyl acrylate (1 g) and
 - 0.13 mmol of dithiocarbamate of formula (H)
- 15 (48 mg).

The tube is closed by a screw stopper and then immersed in an oil bath preheated to 80°C. The polymerization lasts 24 hours.

The polymer is recovered by evaporating the traces of residual monomer and analysed by GPC in THF medium and in polystyrene equivalents. The results are as follows:

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- degree of conversion: 72%,
 - number-average molar mass $M_n = 6000$,
 - polydispersity index $PI = 1.48$.
- 25

Example 2.24: styrene homopolymer

Introduced into a glass tube are:

- 0.013 mmol of AIBN (2.1 mg),
 - 5 - 10 mmol of styrene (1.04 g) and
 - 0.12 mmol of dithiocarbamate of formula (H)
- (48 mg).

The tube is closed by a screw stopper and then immersed in an oil bath preheated to 110°C. The

10 polymerization lasts 24 hours.

The polymer is recovered by evaporating the traces of residual monomer and analysed by GPC in THF medium and in polystyrene equivalents. The results are as follows:

- 15 - degree of conversion: 87%,
- number-average molar mass M_n = 8200,
- polydispersity index PI = 1.23.

Example 2.25: vinyl acetate homopolymer

20

Introduced into a glass tube are:

- 0.003 mmol of AIBN (0.6 mg),
 - 10 mmol of vinyl acetate (1 g) and
 - 0.14 mmol of dithiocarbamate of formula (I)
- 25 (48 mg).

The tube, connected to a vacuum line, is dipped into liquid nitrogen and then three "freezing/vacuum/return to ambient" cycles are carried

out on the contents of the tube so as to degas it. Next, it is vacuum sealed. After returning to ambient, it is immersed in an oil bath preheated to 80°C. The polymerization lasts 28 hours.

5 The polymer is recovered by opening the tube and then evaporating the traces of residual monomer. It is analysed by GPC in THF medium and in polystyrene equivalents. The results are as follows:

- 10 - degree of conversion: 6.6%
- number-average molar mass M_n = 890
- polydispersity index PI = 1.24.

Example 2.26: ethyl acrylate homopolymer

15 Introduced into a glass tube are:

 - 0.003 mmol of AIBN (0.6 mg),

 - 10 mmol of ethyl acrylate (1 g) and

 - 0.13 mmol of dithiocarbamate of formula (I)

(42 mg).

20 After the tube has been filled, it is degassed and vacuum sealed in a manner similar to Example 2.25. The polymerization lasts 64 hours at 80°C.

25 The polymer is recovered by evaporating the traces of residual monomer and analysed by GPC in THF medium and in polystyrene equivalents. The results are as follows:

- degree of conversion: 69%
- number-average molar mass $M_n = 9500$
- polydispersity index $PI = 1.2$.

5

Example 2.27: styrene homopolymer

Introduced into a glass tube are:

- 9.6 mmol of styrene (1 g) and
 - 0.12 mmol of dithiocarbamate of formula (I)
- 10 (40.2 mg).

After the tube has been filled, it is degassed and vacuum sealed in a manner similar to Example 2.25. The polymerization lasts 72 hours at 110°C.

15

The polymer is recovered by evaporating the traces of residual monomer and analysed by GPC in THF medium and in polystyrene equivalents. The results are as follows:

- degree of conversion: 70%
- 20 - number-average molar mass $M_n = 6200$
- polydispersity index $PI = 1.14$.

Example 2.28: vinyl acetate homopolymer

25

Introduced into a glass tube are:

- 0.003 mmol of AIBN (0.6 mg),
- 10 mmol of vinyl acetate (1 g) and

- 0.15 mmol of dithiocarbamate of formula (J)
(56 mg).

After the tube has been filled, it is
degassed and vacuum sealed in a manner similar to
5 Example 2.25. The polymerization lasts 27 hours at
80°C.

The polymer is recovered by evaporating the
traces of residual monomer and analysed by GPC in THF
medium and in polystyrene equivalents. The results are
10 as follows:

- degree of conversion: 25.7%
- number-average molar mass M_n = 2200
- polydispersity index PI = 1.66.

15

Example 2.29: ethyl acrylate homopolymer

Introduced into a glass tube are:

- 0.003 mmol of AIBN (0.6 mg),
- 10 mmol of ethyl acrylate (1 g) and
- 20 - 0.13 mmol of dithiocarbamate of formula (J)
(48 mg).

After the tube has been filled, it is
degassed and vacuum sealed in a manner similar to
Example 10. The polymerization lasts 64 hours at 80°C.

25

The polymer is recovered by evaporating the
traces of residual monomer and analysed by GPC in THF
medium and in polystyrene equivalents. The results are
as follows:

- degree of conversion: 76%
- number-average molar mass $M_n = 6700$
- polydispersity index $PI = 1.2$.

5

Example 2.30: vinyl acetate homopolymer

Introduced into a glass tube are:

- 0.016 mmol of AIBN (2.7 mg),
- 50 mmol of vinyl acetate (4.3 g) and
- 0.62 mmol of dithiocarbamate of formula (K)
(251 mg).

10

After the tube has been filled, it is degassed and vacuum sealed in a manner similar to Example 2.25. The polymerization lasts 41 hours at
15 80°C.

The polymer is recovered by evaporating the traces of residual monomer and analysed by GPC in THF medium and in polystyrene equivalents. The results are as follows:

20

- degree of conversion: 47.8%
- number-average molar mass $M_n = 5000$
- polydispersity index $PI = 1.43$.

25

Example 2.31: ethyl acrylate homopolymer

Introduced into a glass tube are:

- 0.003 mmol of AIBN (0.56 mg),

- 10 mmol of ethyl acrylate (1 g) and
- 0.12 mmol of dithiocarbamate of formula (K) (50 mg).

After the tube has been filled, it is
5 degassed and vacuum sealed in a manner similar to
Example 2.25. The polymerization lasts 21 hours at
80°C.

The polymer is recovered by evaporating the
traces of residual monomer and analysed by GPC in THF
10 medium and in polystyrene equivalents. The results are
as follows:

- degree of conversion: 67%
- number-average molar mass M_n = 5900
- polydispersity index PI = 1.22.

15

Example 2.32: styrene homopolymer

Introduced into a round-bottomed flask are:

- 0.026 mmol of lauroyl peroxide (4.3 mg),
- 20 - 21.3 mmol of styrene (2.22 g) and
- 0.27 mmol of dithiocarbamate of formula (K) (108 mg).

The flask is surmounted by a refrigerant,
placed under a stream of nitrogen and immersed in an
25 oil bath preheated to 115°C. Two new additions of
lauroyl peroxide are carried out after two and four
hours of reaction (0.026 mmol each time). The reaction
is stopped after 24 hours.

The polymer is recovered by evaporating the traces of residual monomer and analysed by GPC in THF medium and in polystyrene equivalents. The results are as follows:

- 5 - degree of conversion: 98%
- number-average molar mass M_n = 6700
- polydispersity index PI = 1.7.

Example 2.33: vinyl acetate homopolymer

10

Introduced into a glass tube are:

- 0.004 mmol of AIBN (0.6 mg),
 - 11.6 mmol of vinyl acetate (1 g) and
 - 0.146 mmol of dithiocarbamate of formula
- 15 (K) (49.8 mg).

After the tube has been filled, it is degassed and vacuum sealed in a manner similar to Example 2.25. The polymerization lasts 100 hours at 60°C.

20

The polymer is recovered by evaporating the traces of residual monomer and analysed by GPC in THF medium and in polystyrene equivalents. The results are as follows:

- 25 - degree of conversion: 71.4%
- number-average molar mass M_n = 5400
- polydispersity index PI = 1.29.

Example 3.1: p(EtA-b-St) block copolymer

- 4.01 g of ethyl acrylate,
- 0.176 g of dithiocarbamate of formula (A)

- 8.8 mg of AIBN.

A small fraction of the polymer obtained is removed and analysed by GPC in THF medium and in polystyrene equivalents:

15 removed and analysed by GPC in THF medium and in polystyrene equivalents:

- degree of conversion: 81.5%
- average molecular mass $M_n = 7300$
- polydispersity index $PI = 1.4$.

- 2.08 g of styrene and
- 4.4 mg of AIBN.

The temperature is raised to 70°C. The polymerization lasts 40 hours.

25 The traces of residual monomer are removed by evaporation and the copolymer is analysed by GPC in THF medium and in polystyrene equivalents:

- 5

1.38 g of the stock solution prepared for Example 3.1 are introduced into a round-bottomed flask. The temperature is raised to 70°C. The polymerization lasts 24 hours after which the traces of residual monomer are removed by evaporation.

15

- Introduced into the flask are:

- 20

The traces of residual monomer are removed by evaporation and the copolymer is analysed by GPC in THF medium and in polystyrene equivalents:

- degree of conversion: 15.6%
- average molecular mass $M_n = 7200$

- polydispersity index $PI = 1.5$.

Example 3.3: p(St-b-EtA) block copolymer

5 A stock solution is prepared from:

- 4.01 g of styrene,
- 0.168 g of dithiocarbamate of formula (A)

and

- 8.3 mg of AIBN.

10 1.00 g of this solution is removed and introduced into a round-bottomed flask. The temperature is raised to 70°C. The polymerization lasts 24 hours after which the traces of residual monomer are removed by evaporation.

15 A small fraction of the polymer obtained is removed and analysed by GPC in THF medium and in polystyrene equivalents:

- degree of conversion: 86.9%
- average molecular mass $M_n = 4500$
- polydispersity index $PI = 1.3$.

Introduced into the flask are:

- 1.92 g of ethyl acrylate and
- 3.7 mg of AIBN.

The temperature is raised to 70°C. The
25 polymerization lasts 40 hours.

The traces of residual monomer are removed by evaporation and the copolymer is analysed by GPC in THF medium and in polystyrene equivalents:

- degree of conversion: 94.8%
- average molecular mass $M_n = 14,100$.
- polydispersity index $PI = 1.7$.

5

Example 3.4: p(EtA-b-St) block copolymer

A stock solution is prepared from:

- 7.5 ml of ethyl acrylate
- 3.9 mg of AIBN (2.4×10^{-3} mol)

10

1.08 ml of this solution are introduced into a glass tube and then 50.5 mg (1.25×10^{-4} mol) of precursor of formula K are added. The contents of the tube are degassed by three "freeze-vacuum-return to ambient" cycles and then vacuum sealed. The tube is then placed for 21 hours in an oil bath maintained at 80°C. At the end of the reaction, the tube is opened and the monomer residues are removed by vacuum evaporation.

The characteristics of the polymer obtained are as follows:

20

- degree of conversion: 67.4%
- average molar mass M_n : 5500
- polydispersity index $PI = 1.22$.

Introduced into a glass tube are:

25

- 0.75 g of styrene
- 1 ml of toluene
- 1.65 mg of AIBN

- 0.5 g of polyethyl acrylate obtained above.

After the tube has been degassed in the same way as that described above, it is vacuum sealed. After 72 hours at 110°C, the tube is opened and the monomer residues are removed by vacuum evaporation.

The characteristics of the copolymer obtained are as follows:

- degree of conversion: 49.4%
- average molar mass M_n : 8500
- polydispersity index: $PI = 1.34$.

Example 3.5: p(EtA-b-St) block copolymer

A stock solution is prepared from:

- 5.4 ml of ethyl acrylate
- 3 mg of AIBN (2.4×10^{-5} mol)

1.08 ml of this solution are introduced into a glass tube and then 41.8 mg (1.1×10^{-4} mol) of precursor of formula I are added. The contents of the tube are degassed by three "freeze-vacuum-return to ambient" cycles and then vacuum sealed. The tube is then placed for 21 hours in an oil bath maintained at 80°C. At the end of the reaction, the tube is opened and the monomer residues are removed by vacuum evaporation.

The characteristics of the polymer obtained are as follows:

- degree of conversion: 69.7%
- average molar mass M_n : 7050
- polydispersity index $PI = 1.2$.

Introduced into a glass tube are:

5

- 1 g of styrene
- 1 ml of toluene
- 2 mg of AIBN
- 0.72 g of polyethyl acrylate obtained

above.

10

After the tube has been degassed in the same way as that described above, it is vacuum sealed. After 72 hours at 110°C, the tube is opened and the monomer residues are removed by vacuum evaporation.

The characteristics of the copolymer obtained
15 are as follows:

- degree of conversion: 26.1%
- average molar mass M_n : 12,900
- polydispersity index: $PI = 1.29$.

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